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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : A23L 1/221 — A1

(11) International Publication Number: WO 92/09210

(43) International Publication Date: 11 June 1992 (11.06.92)

(21) International Application Number: PCT/US91/08719

(22) International Filing Date: 21 November 1991 (21.11.91)

(30) Priority data:
616,510 21 November 1990 (21.11.90) US

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(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent).

Published
With international search report.

(54) Title: POLYHYDROXYALKANOATE FLAVOR DELIVERY SYSTEM

(57) Abstract

Polyhydroxyalkanoates are combined with fat soluble flavors to provide a flavor delivery system for low-fat and no-fat foods. The polyhydroxyalkanoates preferably have a porous structure.

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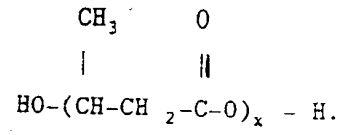
POLYHYDROXYALKANOATE FLAVOR DELIVERY SYSTEM

BACKGROUND OF THE INVENTION

The present invention relates to the use of polyhydroxyalkanoate compositions (PHA) as a flavor delivery system for low-fat and no-fat foods products. Additionally, the present invention relates to a method of delivering fat soluble flavors to low-fat and no-fat food products by combining PHAs with fat soluble flavor compound and then adding the combination to the low-fat or no-fat food. The PHA/flavor composition provides release of fat soluble flavors similar to that of the traditional fat laden food counterparts. Additionally, the present invention relates to non-fat and low-fat food products which contain the present flavor delivery system.

Poly(hydroxyalkanoates) (PHAs) are well-known polyester compounds produced by a variety of microorganisms, such as bacteria and algae. A PHA polyester can include the same or different repeating units, depending upon the choice of carbon source substrates and fermentation conditions employed in the production of the PHA. One particular PHA including the same repeating units is poly(3-hydroxybutyric acid), or poly(3-hydroxybutyrate), termed PHB, and having the structural formula:



wherein x represents an integer of from 500 to about 16,000.

PHB is a natural storage product of bacteria and algae, and is present as discrete granules within the cell cytoplasmic space. However, unlike other, biologically-synthesized polymers such as proteins and polysaccharides, PHB is thermoplastic having a high degree of crystallinity and a well-defined melting point at about 180°C. But, PHB is unstable at its melting point and

degrades, essentially quantitatively, to crotonic acid at a temperature slightly above its melting point. Accordingly, practical applications for this natural, biodegradable polyester have been limited. Therefore, investigators have studied other PHAs, such as the biodegradable copolyester poly(hydroxybutyrate-co-valerate), including both of the monomeric units 3-hydroxybutyrate and 3-hydroxyvalerate, in order to discover a PHA having sufficient thermal stability and other suitable chemical and physical properties for use in practical applications.

Generally, a PHA is synthesized by a microorganism. However, some PHA compounds have been synthesized chemically, such as by polymerization of racemic and optically-active butyrolactone or other suitable monomers. Such chemically-synthesized PHA polyesters exhibit a relatively low average molecular weight, and the synthesis is not economically viable. In general, the following publications provide background information for PHA polymers, both in regard to their synthesis and their properties:

1) E.A. Dawes, et al., Adv. Microb. Physiol., 10, p. 135 (1973);

2) P.A. Holmes, "Developments in Crystalline Polymers-2", D.C. Basset, ed., Elsevier Applied Science, London, Chap. 1, pp. 1-65 (1988); and

3) P.A. Holmes, Phys. Technol., 16, pp. 32-36 (1985).

The preparation, extraction and purification, of a PHA by a biosynthetic process is known. For example, Richardson in European Patent Application Serial No. 046,344, and Lafferty et al. in U.S. Patent No. 4,786,598, disclose the preparation of poly-D-(-)-3-hydroxybutyric acid (PHB) by culturing the microorganism Alcaligenes latus or a mutant thereof. Walker et al., in U.S. Patent No. 4,358,583, teach the extraction and purification of poly(3-hydroxybutyric acid) from the cells walls of PHB-producing microorganisms. Furthermore, the bacterial synthesis of various co-poly(hydroxyalkanoates), such as the copolymer of 3-hydroxybutyric acid and 3-hydroxypentanoic acid, is described in publications such as:

Y. Doi, et al., "Production of Copolyesters of 3-Hydroxybutyrate and 3-Hydroxyvalerate by Alcaligenes eutrophus from Butyric and Pentanoic Acids", Appl. Microbiol. Biotechnol., 28, pp. 330-334 (1988);

Doi, U.S. Patent No. 4,876,331;

P. Holmes, Phys. Technol., 16, pp. 32-36 (1985);

M. Kunioka, et al., "Crystalline and Thermal Properties of Bacterial Copolyesters: Poly(3-Hydroxybutyrate-co-3-hydroxyvalerate) and Poly(3-Hydroxybutyrate-co-4-hydroxybutyrate)", Macromolecules, 22, pp. 694-697 (1989); and

R. Gross, et al., "Biosynthesis and Characterization of Poly(s-Hydroxyalkanoates) Produced by Pseudomonas oleovorans", Macromolecules, 22, pp. 1106-1115 (1989).

The above-listed patents and publications are representative of the state of the art relating to PHAs. In general, the homopolymeric and copolymeric PHAs described in the above references are attempts to improve the physical and chemical properties of the PHA by altering the carbon source for the biological synthesis of the PHA, or are attempts to find a suitable microorganism to produce a sufficient amount of the desired PHA. In general, a poly(hydroxyalkanoate) has the general structural formula (I), wherein R is hydrogen or an alkyl group having 1-9 carbon atoms, and the term "a" is the number of repeating units. As illustrated in general structural formula (I), a PHA is a polyester having a hydroxy-terminated end and a carboxy-terminated end. The most widely-known and intensively-studied

$$HO\text{-}(CHCH_2COO\text{-})_xH \qquad (I)$$

poly(hydroxyalkanoate) is the previously-described, biodegradable PHA known as poly(hydroxybutyrate), or PHB, wherein the R substitutent in general structural formula (I) is methyl. However, PHAs having an R substituent of up to nine carbon atoms

have been biosynthesized and studied, as have PHAs including 4-hydroxybutyrate [(-$CH_2CH_2CH_2CO$-)n] as a repeating unit.

In addition, copolymers of general structural formula (II) have been biosynthesized by the appropriate choice of carbon substrates. For example, the copolymer of general structural formula (II), wherein

$$HO\text{-}(CHCH_2COO)b(CHCH_2COO)c\text{-}H \qquad (II)$$
(with R_4 above the first CH and R_5 above the second CH)

R_4 is methyl and R_5 is ethyl, known as poly(hydroxybutyrate-co-valerate) or (P[HBcoHV)), has been biosynthesized and studied. In general, the copolyesters of general structural formula (II) wherein the substituents R_4 and R_5 independently, are hydrogen or an alkyl or alkenyl group including up to nine carbon atoms are known. Alkenyl-branched PHA's are described by K. Fritzsche, in "Production of Unsaturated Polyesters by Pseudomonas oleovorans", Int. J. Biol.Macromol., Vol. 12, pp. 85-91 (1990). In addition, a terpolymer of structural formula (III) has been biosynthesized by the bacterium Rhodospirillum rubrum from a carbon source including 3-hydroxybutyric acid, 3-hydroxypentanoic acid and 4-pentenoic acid.

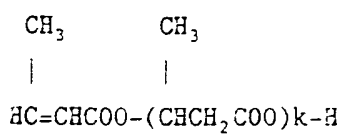
$$H\text{-}[O\text{-}CHCH_2CO_2]d\text{-}[CHCH_2CO_2]e\text{--}[CHCH_2CO_2]_x\text{-}H \qquad (III)$$
(with $CH{=}CH_2$, CH_3, and $CHCH_3$ above the respective CH groups)

This terpolymer is described by R. Gross et al. in the publication, "The Biosynthesis and Characterization of New Poly(e-Hydroxyalkanoates)", in Polymer Preprints, 30(1), pp. 492-493 (1989).

The biologically-synthesized PHAs exhibit a molecular weight of up to about 1,500,000 daltons. These high molecular weight, biologically-synthesized PHAs can be degraded, or depolymerized, to yield a PHA having a molecular weight as low as about 3000

daltons. For example, Trathnigg et al., in Angew. Macromol. Chem., 161, p. 1-8 (1988), described the preparation of a low molecular weight PHB by a controlled acid hydrolysis of a high molecular weight, biologically-synthesized PHB using aqueous formic, acetic or butyric acid at an elevated temperature of 90-100°C. Similarly, B. Heuttecoeur, et al., in C.R. Hebd. Seances Acad. Sci., 274, pp. 2729-2732, (1972), describe the partial alkaline degradation of PHB, and S. Akita, et al., in Macromolecules, 9, pp. 774-780 (1976), describe the alcoholysis of PHB with methanol and p-toluenesulfonic acid. The methods of Trathnigg, et al and Heuttecoeur, et al provide a degraded PHB polymer with a carboxylic acid or a carboxylate terminal group, whereas the method of Akita provides an ester terminal group. Also see S. Coulombe, et al., "High-Pressure Liquid Chromatography for Fractionating Oligomers from Degraded Poly(s-Hydroxybutyrate)", Macromolecules, 11, pp. 279-280 (i978); and A. Ballistreri, et al., "Sequencing Bacterial Poly(s-Hydroxybutyrate-co-o-hydroxyvalerate) by Partial Methanolysis, High-Performance Liquid Chromatography Fractionation and Fast Atom Bombardment Mass Spectrometry Analysis", Macromolecules, 22, pp. 2107-2111 (1989).

H. Morikawa et al. in Can. J. Chem., 59, pp. 2306-2313, (1981) demonstrated that thermal degradation of a PHA copolyester yields monomeric, oligomeric and polymeric PHAs with olefinic terminal groups. Morikawa et al. pyrolyzed PHB to yield crotonic acid and oligomers of PHB having a terminal crotonate moiety, as shown in the polyester of structural formula (IV). Therefore, pyrolysis of a PHA can provide an



(IV)

oligomer with a reactive vinyl terminal group as a site for further chemical modification of the degraded PHA.

Accordingly, from the above degradation methods, i.e. acidic hydrolysis, alkaline hydrolysis, alcoholysis or pyrolysis, a high molecular weight, biologically-synthesized PHA can be degraded to a relatively low molecular weight PHA that includes one of a variety of reactive terminal functionalities, including hydroxyl, free carboxylic acid, carboxylate, ester, and olefinic functionalities. These reactive terminal functionalities therefore allow the introduction of numerous other types of terminal functionalities onto the degraded PHA polyester.

In the past, interest in PHAs concentrated on their unique biodegradable and biocompatible properties, as well as their various physical properties that range from thermoplastic to elastomeric. The physical and chemical properties inherent to PRAs suggest a variet of applications, such as in controlled drug release systems, biomedical devices, specialty packaging materials, and numerous agricultural applications. However, while PHAs are of general interest because of their biodegradable nature, their actual use as a plastic material has been hampered by their thermal instability. For example, poly-3-hydroxybutyrate is thermoplastic, but also is thermally unstable at temperatures exceeding its melting point of about 180° C. N. Grassie, et al., in Polym. Degrad. Stabil., 6, pp. 47-61 (1984), disclose that a substantial molecular weight reduction of PHB occurs by heating PHB in the temperature range of 180-200°C. The inherent thermal instability of PHB is partially overcome by incorporating a second monomer unit into the polyester. The melting point of a PHB can, for instance, be reduced to 75° C, as in (P[HBcoHV)) including about 40 mol % 3-hydroxyvalerate, resulting in a polymer that is thermally stable up to about 160° C. However, further enhancements in the thermal stability of PHAs are necessary for their practical use in commercial applications. Also see M. Kunioka, et al., Macromolecules, 23, pp. 1933-1936 (1990).

Accordingly, prior investigators have studied the chemical and biological synthesis of PHAs, and the degradation of PHAs, in attempts to provide a biodegradable polymer having physical and chemical properties suitable for consumer, industrial and agricultural applications. However, the prior investigators have studied essentially only homopolymeric and copolymeric hydroxyalkanoates. In general, to date, very few known references are directed to a compound, or its method of preparation, including a PHA polymer functionalized with a moiety other than a poly(hydroxyalkanoate).

Some investigators, like P.B. Dave et al., in "Survey of Polymer Blends Containing Poly(3-Hydroxybutyrate-co-16% Hydroxyvalerate", in Polymer Preprints, 31(1), pp. 442-443 (1990), studied the physical compatibility of a PHA blended with other commercial polymers. However, these were physical blends of a PHA with a second polymer, like a poly(ethylene oxide), and did not include a PHA polymer covalently attached to a molecule or a polymer other than a PHA. R.I. Hollingsworth et al. in Carbohydrate Research, 134, pp. C7-C11 (1984) and R.I. Hollingsworth et al. in Journal of Bacteriology, 169(7), pp. 3369-3371 (1987) found 3-hydroxybutyrate covalently attached as a noncarbohydrate substituent in the acidic capsular polysaccharide and extracellular polysaccharide of Rhizobium trifolii. However, the 3-hydroxybutyrate substituent was monomeric and was substituted biologically, not chemically. M.S. Reeve et al., in "The Chemical Degradation of Bacterial Polyesters for Use in the Preparation of New Degradable Block Copolymers", Polymer Preprints, 31(1), pp. 437-438 (1990), disclose a polyurethane-type copolymer derived from the reaction of 4,4'-diphenylmethane diisocyanate with polyethylene glycol and degraded PHB, and disclose a PHB-polystyrene block copolymer derived from degraded PHB and a polystyrene prepolymer including a carboxylic acid functionality.

SUMMARY OF THE INVENTION

Briefly, in accordance with the present invention, a flavor delivery composition is prepared by combining fat soluble flavor compositions with polyhyroxyalkanoates (PHA). The present flavor delivery compositions are added to low-fat and no-fat foods to provide the fat soluble flavoring to the food. The release of the fat soluble flavors is similar to that of high-fat content foods and provides the natural taste impression of conventional full-fat food products. The present flavor delivery compositions can be used to flavor low/no fat food products such as ice cream, yogurt, salad dressings, mayonnaise, cream, cream cheese, other cheeses, sour cream, sauces, icings, whipped toppings, frozen confections, dairy drinks and spreads.

Of particular interest, PHB and P(HBcoHV) are admixed with fat soluble flavors to form porous particles having a particle size distribution of from about 0.1-200 microns (μ).

DETAILED DESCRIPTION OF THE INVENTION

In practicing the present invention, fat soluble flavors and PHAs, are admixed and added to low-fat or no-fat fat/cream-containing food products as a flavoring component. The resulting food products have the natural taste impression of their fatty counterparts. The flavor is then released in a more natural and familiar sequence and rate as the PHA/flavor composition is warmed by the mouth, thereby generating a more natural temporal flavor profile which is characteristic of the flavor profile of conventional high-fat foods. Water soluble flavor components, on the other hand, are readily released in low or non-fat foods for sensory perception resulting in the usual pattern of perception for such components since this process doesn't impede or perturb their pattern of release. Therefore, by employing the present flavor delivery compositions, the fat soluble flavor sensation of full fat foods is achieved without the incorporation of fat. Suitable fat soluble flavors include

vanilla extract, vanillin, starter distillates, lipolyzed oils, botanical extracts, natural and artificial fatty flavors. Mixtures of fat soluble flavors can also be employed in the practice of the present invention.

Any naturally harvested or synthetically produced PHA is acceptable in practicing the present invention. Suitable PHAs include PHB and P(HBcoHV). The PHA can also be a copolymer of hydroxybutyrate and a C_2-C_{12} alkanoate. Mixtures of different PHAs can also be employed. Preferred PHAs include those having a porous surface. The PHAs and fat soluble flavors can be combined in any manner. They can be physically mixed together employing standard mixing techniques. Preferably, the fat soluble flavors are mixed with soluble PHAs prior to precipitation of the PHA into a solid particle, sheet or film, thereby providing a flavor delivery composition comprising a uniform dispersion of fat flavor and PHA. Especially, preferred compositions are those where the PHA exhibits a porous shape which have fat flavors dispersed throughout the porous PHA.

The following Examples illustrate the practice of the present invention, but should not be construed as limiting its scope.

EXAMPLE 1: POLY(HYDROXYBUTYRATE)/POLY(HYDROXYVALERATE) AS A FLAVOR CARRIER

Poly(hydroxybutyrate)/poly(hydroxyvalerate) (14% PHV) was added to methylene chloride at 6.67% w/v and the suspension refluxed until the polymer was completely dissolved (~30 minutes). Upon cooling the PHBV/CH_2Cl_2 solution, 1% w/v of vanillin was added and the mixture was stirred until clear. This solution was poured into 0.1M sodium phosphate, pH 7.4, containing 1% w/v gelatin, at a ratio of 1 part polymer/flavor solution to 50 parts aqueous buffer, while stirring at 600 - 650 RPM. After ~20 minutes, stirring was reduced to 550 RPM (due to foaming) and continued for 1.5 hours, in a hood, so that the methylene chloride evaporated. The "microspheres" were collected

on a fritted funnel, washed with a copious amount of water and lyophilized.

Functionality as a flavor delivery system was measured in two runs on a 10% w/v suspension of the PHBV/vanillin in water. The amount of free vanillin was measured by HPLC at 25°C before warming the suspension to higher temperatures (37°C, 50°C and 70°C) and monitoring the vanillin concentration as a function of time. The vanillin measurements were carried out by injecting 100ml of supernatant onto a reversed phase C18 column (250mm x 4.6mm) using 20:80 acetonitrile/water, at a flow rate of 1ml/min, as the mobile phase. Detection was achieved by measuring the change in absorbance at 348nm.

The amount of measurable vanillin increased significantly as the temperature was raised from 25°C to 37°C, and more than when heated to 50°C as illustrated in TABLES 1 and 2. Free vanillin decreased when the temperature was taken to 70°C.

Table 1. Vanillin Release Results From Incubation Run #1

Incubation Temp. (°C)	Incubation Time (min)*	Peak Area (MV°sec)
25	2	1080
25	30	1376
25	45	1440
25	60	1580
heated		
50	20	2752
50	40	3215
50	60	3263
50	2460	3796

* Time of incubation at that particular temperature.

Table 2. Vanillin Release Results From Incubation Run #2

Incubation Temp. (°C)	Incubation Time (min)*	Peak Area (MV°sec)
25	2	386
25	20	668
25	40	755
25	60	790
heated		
37	20	1126
37	45	1449
37	60	1611
37	1005	2135
heated		
50	30	2758
50	60	2791
50	120	3107
heated		
70	30	2544
70	60	1671

* Time of incubation at that particular temperature.

As can be seen from the results, the amount of free vanillin (vanillin in solution) increased significantly as the temperature was increased to as high as 50°C.

Scanning electron micrographs of the PHBV/flavor composition of the present invention were compared to spray dried PHBV as purchased from Aldrich Chemical Co. The Aldrich material was composed of spherical particles ranging from 0.46 to 1.9 microns in size and were highly aggregated as seen in Fig. 1. The PHBV/flavor particles were not aggregated, appeared hollow, were much larger in size and appeared to have a much more porous surface structure. They ranged from 15.4 to 126.9 microns as seen in Fig. 2.

EXAMPLE 2

PHBV/vanillin microspheres were prepared as described in EXAMPLE 1, with the exception that 2% w/v vanillin was added to the 6.67% w/v PHBV/CH_2Cl_2 solution. Also, the PHBV/vanillin solution was added to the aqueous buffer at a ratio of 1:13.3. All other steps for the preparation of the microspheres were identical.

Flavor delivery was evaluated, as described in EXAMPLE 1, on a 5% w/v suspension of the PHBV/vanillin in four systems, i.e. (i) water; (ii) a full-fat frozen dessert mix; (iii) a low-fat frozen dessert mix containing SIMPLESSE brand fat substitute; and (iv) a frozen dessert mix negative control containing no fat or fat substitute ingredient. The vanillin measurements were carried out by centrifuging aliquots of the respective mixes, diluting the supernatants at 1:1 with a solution of 70:30 acetonitrile/water, then centrifuging and injecting 100ul aliquots of the supernatents onto the HPLC system described above.

From the results listed in Tables 3-6, it is evident that the amount of free vanillin increased significantly in all four systms as the samples were warmed from 5°C to 37°C.

Table 3. Vanillin Release Results From Incubation of PHBV/vanillin in Water

Incubation Temp. (°C)	Incubation Time (min)*	Peak Area (MV°sec)
5	40	1814
5	60	2016
5	90	2247
heated		
37	30	3771
37	60	6466
37	90	7330

* Time of incubation at that particular temperature.

Table 4. Vanillin Release Results From Incubation of PHBV/vanillin in Full Fat Frozen Dessert Mix

Incubation Temp. (°C)	Incubation Time (min)*	Peak Area (MV°sec)
5	20	2158
5	40	1663
5	60	3061
5	90	1460
5	120	1971
heated		
37	30	6053
37	60	5570
37	90	6537

* Time of incubation at that particular temperature.

Table 5. Vanillin Release Results From Incubation of PHBV/vanillin in Frozen Dessert Mix Containing Simplesse fat substitute

Incubation Temp. (°C)	Incubation Time (min)*	Peak Area (uV*sec)
5	20	1632
5	40	720
5	60	1081
5	120	1692
heated		
37	30	6952
37	90	10112
37	240	10810

* Time of incubation at that particular temperature.

Table 6. Vanillin Release Results From Incubation of PHBV/vanillin in No Fat/No Fat Substitute Frozen Dessert Mix

Incubation Temp. (°C)	Incubation Time (min)*	Peak Area (uV*sec)
5	20	1107
5	40	1844
5	60	1158
5	90	1532
heated		
37	30	2128
37	60	5091
37	90	5630

* Time of incubation at that particular temperature.

It should be noted, that Frozen Dessert mix which contained SIMPLESSE fat substitute was injected onto the HPLC system after diluting 1:1 with a solution of 70:30 acetonitrile/water and centrifuging. The peak areas for duplicate runs were 4902 and 3792 uV°sec respectively. See Juni, Nakano and Kubota, "Journal of Controlled Release", 4 (1986) 25-32

In similar embodiments the various PHA compositions described herein are combined with fat flavors to provide a flavor delivery system for low-fat and no-fat foods.

Additionally the present PHA compositions can be combined with colors, natural or artificial to stabilize the release of color and provide heat stability to heat sensitive colors.

WHAT IS CLAIMED IS:

1. A method for the delivery of fat soluble flavor compounds into nonfat and low-fat food products in which fat components have been replaced by non-lipid fat substitutes comprising the step of introducing into said food products a composition comprising

(a) fat flavors and

(b) a polyhydroxyalkanoate of the formula

$$\mathrm{HO - (\overset{\overset{\textstyle R}{|}}{C}HCH_2COO-)_x\ H}$$

wherein R represents a C_1-C12 alkyl which can be the same or different on each repeating monomeric unit and x represents an interger of from 500 - 17,000.

2. The method of claim 1 wherein the PHA is a homopolymer.

3. The method of claim 2 wherein R is methyl.

4. The method of claim 1 wherein the PHA is a copolymer of hydroxybutyrate and hydroxyvalerate.

5. The method of claim 1 wherein the PHA is a copolymer or terpolymer.

6. The method of claim 1 wherein the PHA is a copolymer of hydroxybutyrate and a C_2-C_{12} alkonoate.

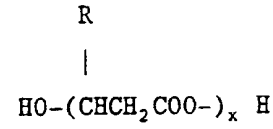
7. The method of claim 1 wherein said flavor compounds are selected from the group consisting of vanilla extract,

vanillin, starter distillates, lipolyzed oils, botanical extracts, natural and artificial fatty flavors.

8. In a food product containing a fat and/or cream, the improvement which comprises adding to food product a flavor delivery system which comprises:

(a) fat soluble flavors

(b) PHA particles of the formula



wherein R represents a C_1-C_{12} alkyl which can be the same or differnet on each repeating monomeric unit and x represents an interger of from 500 - 17,000.

9. The improved food product of claim 8 which is ice cream, yogurt, salad dressing, mayonnaise, cream cheese, cheese, milk, an icing, a spread, sour cream, coffee whitener, whipped topping, cream, or a sauce.

10. The improved food product of claim 9 which is ice cream.

11. The improved food product of claim 9 which is salad dressing.

12. The improved food product of claim 8 wherein the PHA is a homopolymer.

13. The improved food product of claim 8 wherein R is methyl.

14. The improved food product of claim 8 wherein the PHA is a copolymer of hydroxybutyrate and hydroxyvalerate.

15. The improved food product of claim 8 wherein the PHA is a copolymer or terpolymer.

16. The improved food product of claim 8 wherein the PHA is a copolymer of hydroxybutyrate and a C_2-C_{12} alkanoate.

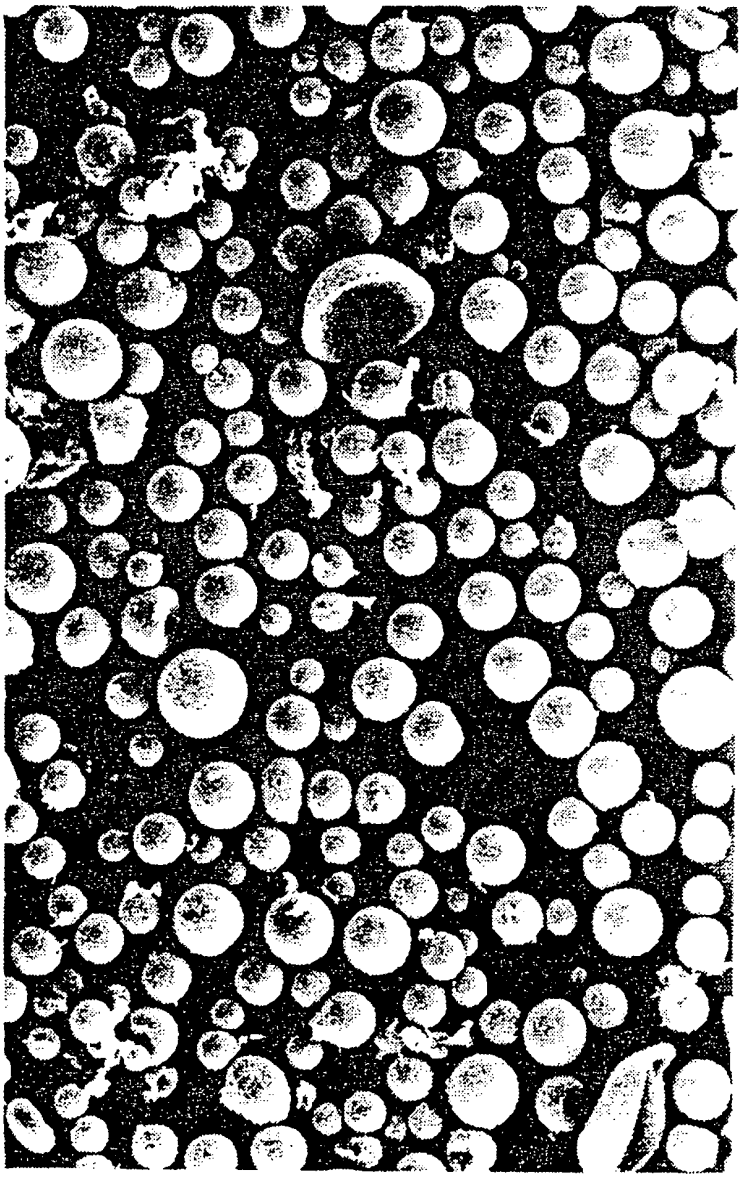


FIG. 1

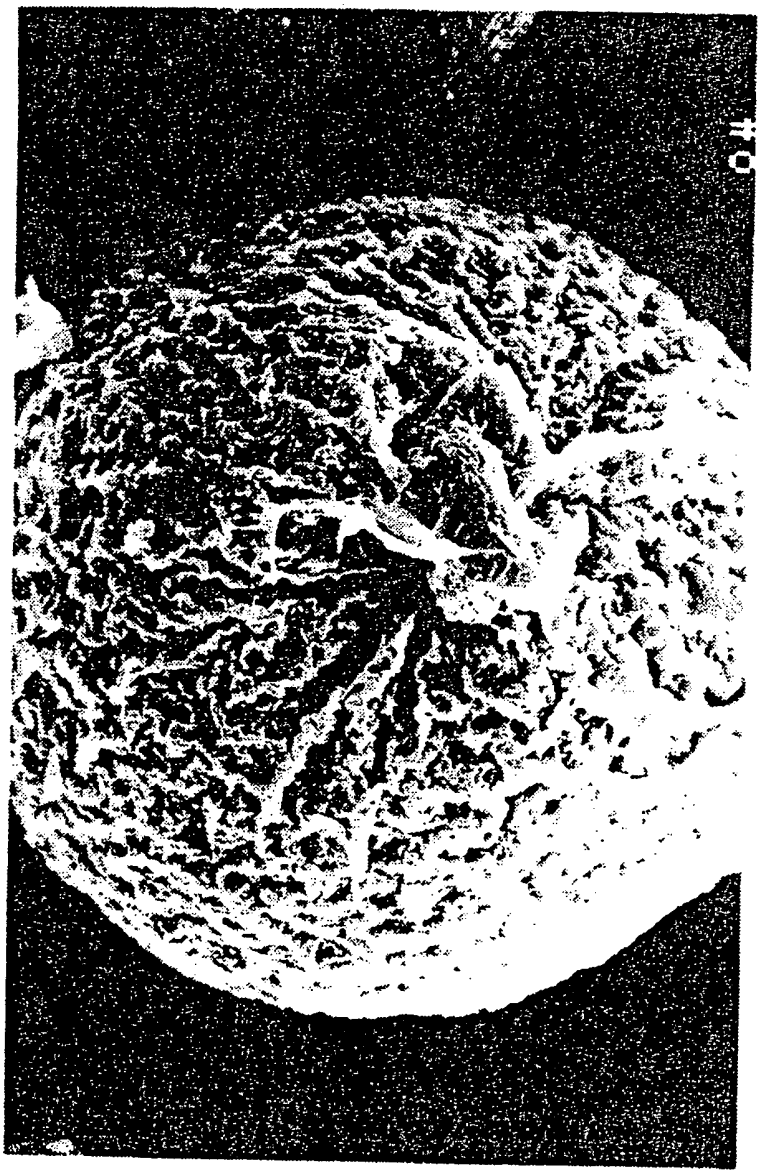


FIG. 2

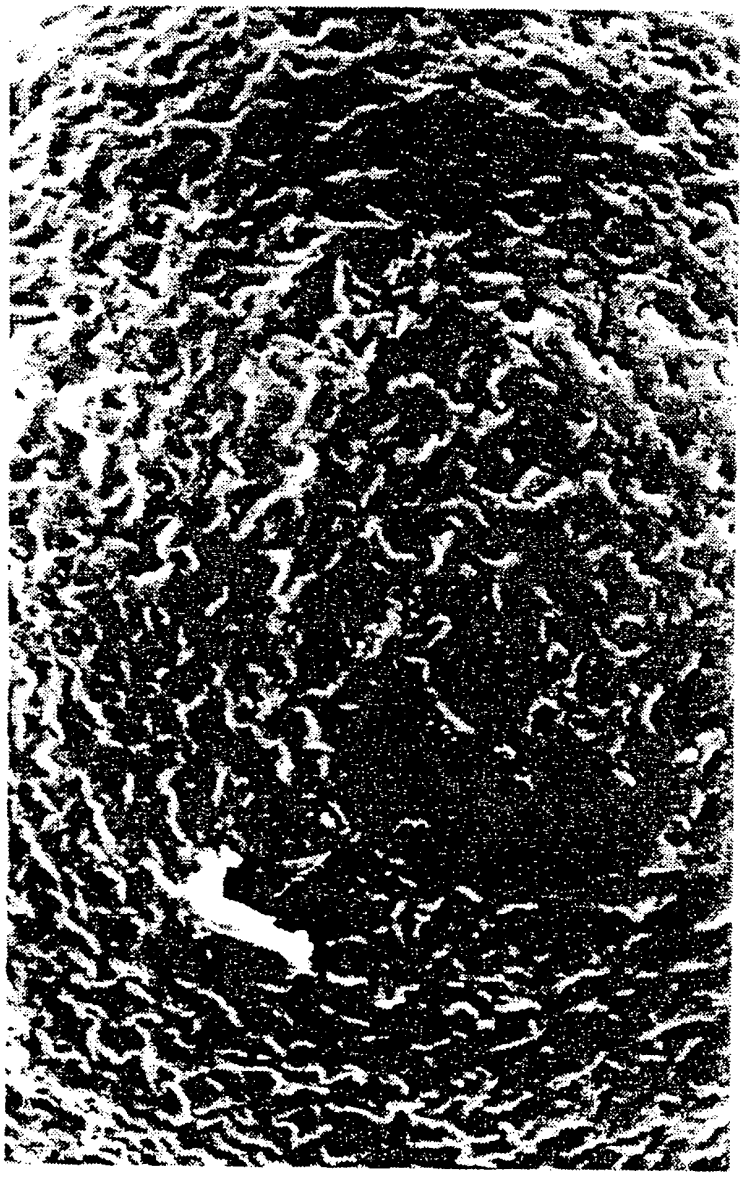


FIG. 3

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/08719

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (5): A23L 1/221

U.S.Cl.: 426/531,534,565,566,572,582,583,586,589,601,605,611,804

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
U.S.Cl.	426/531,534,565,566,572,582,583,586,589,601,605,611,804

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	Patledge, "Liped Biotechnology A wonderland for the microbial physiologist", Journal of The American Oil Chemists Society Vol. 64 #12 Abstract 1987.	
A	US, A, 4,358,583 (WALKER ET AL.) 09 November 1982	
A	US, A, 4,705,604 (VANLAUTEM ET AL.) 10 November 1987	
A	US, A, 4,786,598 (LAFFERTY ET AL.) 22 November 1988	

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
21 February 1992	13 MAR 1992
International Searching Authority	Signature of Authorized Officer
ISA/US	Evan Federman

Form PCT/ISA/210 (second sheet) (Rev.11-87)